

CHANGE IN PHYSICAL AND CHEMICAL CHARACTERISTICS OF BROWN COAL ALONG WITH A PROGRESS OF MOISTURE RELEASE

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INTRODUCTION

Low rank coals, such as lignite and brown coal, have high residual moisture contents in the range of 30-70wt% [1]. Due to such a high moisture content of the coal, moisture removal is the first and essential step in almost any process for upgrading or utilizing them. Since the moisture removal is known to have a significant effect on the physical and chemical properties of dried coal, fundamental understanding of moisture removal is of some consequence. It would be easy to imagine that the effects are brought about by the change in macromolecular structure of coal along with moisture release [2]. Although it is considerable that the physical change of coal during drying process is caused by the change in macromolecular structure of the coal, the natures of macromolecular structure of coal have not been fully understood. Recently, computer-aided molecular design (CAMD) technique has applied to the area of fuel chemistry to obtain insight into the structure, properties and interactions of macromolecules. Carlson has determined three-dimensional minimum-energy conformation of four bituminous coal models, and indicated that nonbonding interactions, in particular, van der Waals and hydrogen bonding interactions, are strong driving forces to form and stabilize the three-dimensional structure of the coal models [3]. Takanohashi and co-workers determined the minimum-energy conformation of bituminous coal by CAMD and reported that the bituminous coal has a possibility to have associated structure of coal molecules which have a continuous distribution of molecular weight [4,5]. In the present study, the conformational change in macromolecular structure of an Australian brown coal with its moisture removal process was simulated by means of a CAMD method.

EXPERIMENTAL

CAMD calculation method

The CAMD study was carried out using PolyGraf software. The software allows treatment of relatively large molecules containing up to 20 000 atoms and is capable of calculating the most stable structures with the minimum conformational energies using AMBER, MM2 and DREIDING force fields. In this study, the DREIDING force field was used. The energy for model molecule was evaluated from forces of bonded interactions (bond; E_b , angle; E_a , torsion; E_t , inversion; E_i), and forces of non-bonded interactions (van der Waals; E_{vdw} , electrostatic; E_{el} , hydrogen bond; E_{hb}), as follow:

$$E = (E_b + E_a + E_t + E_i) + (E_{vdw} + E_{el} + E_{hb})$$

The structure of Yallourn brown coal (YL) was modeled by two oligomers, namely a tetramer (Mw=1540) and a pentamer (Mw=1924), of unit structure. The unit structure which was constructed on the basis of the data from elemental analysis and ¹³C-NMR spectroscopy of the coal is shown in figure 1. Each oligomer was specially arranged so as to have no interaction with others. Simulations of moisture removal process were initiated by generating 360 water molecules (65.25wt%, wet basis) surrounding the model molecule and the minimum energy conformation (MEC) for the model with water molecules was calculated based on molecular mechanics and molecular dynamics methods. After MEC was obtained, the potential energies and volume were calculated individually for the model molecule with water and model molecule alone. The volume was defined as the void volume using water as a probe molecule. The

calculation was repeated decreasing the number of water molecules step by step to 0, and finally MINEC for model molecule with 0 water, i.e., completely dried coal was obtained. Re-adsorption of water onto the completely dried coal was also simulated in the same manner by generating 360 water molecules surrounding the model molecule with 0 water.

Coal Sample

Yallourn brown coal (YL, Moisture;60.0wt% wet basis, ash; 1.1wt% dry basis, C;62.6wt%, H;4.6wt%, N;0.7wt%, S;0.3wt%, O;31.6wt% diff.) was selected and used as a sample. The moisture content of the sample coal was controlled by varying the relative humidity in a vessel from 0 to 84% at 303K using conc. H_2SO_4 and aqueous solutions saturated by selected salts.

Volumetric Change Measurements

For coal drying process, partially and completely dried brown coal samples were placed in constant diameter tubes (8 mm i.d.), then centrifuged for 5 min at 4 500 rpm. After which the height of the coal particle bed was measured by caliper. For volumetric recovery measurement, water was added in the tube containing completely dried sample, then the contents were vigorously stirred. The tube was sealed and placed in an oven kept at 303K for 7 days. The tube was centrifuged again for 5 min at 4 500 rpm, then the height of coal bed was measured. The volumetric shrinkage of sample during moisture release process was determined by referring to the initial volume of as received sample. The volumetric recovery of dried sample was determined by referring to the initial volume of as received sample.

RESULTS AND DISCUSSIONS

The volumetric change of the YL during moisture release process was determined. The results are shown in figure 2 as a function of the extent of moisture removal. During moisture release process, the volume decreases monotonously with moisture removal, and reaches nearly a half of initial volume at the final stage. The volumetric recovery for completely dried brown coal was also determined. The volume of the completely dried sample is not recoverable with moisture re-adsorption. These results reveal that the volumetric change of YL is irreversible when the moisture is removed completely from the coal and imply that the irreversibility is caused by conformational change in the macromolecular structure of the coal during moisture release process. In order to elucidate the conformational change, CAMD technique has been applied for simplified brown coal model molecule.

Volumetric change in MEC of YL model molecule during moisture release process obtained with CAMD calculation is shown in figure 3. The MEC were extracted after 100 pico-second molecular dynamics calculation. The calculated volume for MEC of YL model molecule with water molecules, here after defined as *COAL/WATER*, shows monotonous decrease with moisture removal. The volumetric changes of *COAL/WATER* well corresponded to the experimentally observed volumetric changes of YL. The conformation for MEC of YL model molecule alone, defined as *COAL*, showed an extensive shrinkage of the size from the initial expanded to the contracted as well as deformation of the shape with a decrease in the number of water molecules. The volume for *COAL* remains constant with the extent of moisture removal up to 60%. A significant decrease in *COAL* volume is observed with the extents higher than 80%, resulting in a completely dried *COAL* with a volume being 80% of the initial one. For re-adsorption of water molecules onto the completely dried coal, *COAL/WATER* recover its volume by 85% of the initial one. The volume of *COAL*, however, is not affected by moisture re-adsorption. These CAMD calculation results indicate that removal of water molecules is responsible for the volumetric change of *COAL/WATER* with progress of moisture release, and change in the conformation of *COAL* proceeds in the final stage of moisture release. Also, the conformational change is irreversible and re-adsorption of water molecules causes an increase in coal volume without affecting the coal conformation.

The total potential energies for *COAL/WATER* ($E_{C/W}$) can be assumed as a sum of three potential energies, i.e. *COAL* (E_C), water molecules (E_w) and interaction between brown coal model

molecule and water molecules (E_{NT}), as follow;

$$E_{\text{C/W}} = E_{\text{C}} + E_{\text{W}} + E_{\text{NT}}$$

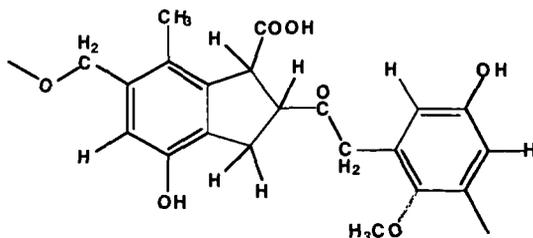
Figure 4 shows the change in $E_{\text{C/W}}$ and E_{C} as a function of moisture removal. Monotonous increase in $E_{\text{C/W}}$ clearly indicates the marked contribution of water molecules on the stabilization of *COAL/WATER*. The stabilization could be attributed to the non-covalent interactions among water molecules and between YL model molecule and water molecules. E_{C} decreased drastically for the extent of moisture removal of 80% and the change corresponded well to the volumetric change of *COAL*. The decrease of E_{C} suggests the stabilization of *COAL*, whereas the increase of $E_{\text{C/W}}$ means that *COAL/WATER* becomes unstable along with moisture release process. For moisture re-adsorption, E_{C} shows incomplete recover, since $E_{\text{C/W}}$ reverts completely to its initial value. This means that the YL model molecule has most stable conformation at completely dried state. While the effects of moisture release on the conversion reactivity thought to be due to a physical change, such as collapse of pores, the stabilization of the macromolecular structure also makes contributions to the conversion reactivity. In summary, the change in conformation for YL model molecule with its moisture release process could be successfully simulated by using the CAMD method. Although the coal model molecule employed in this study is rather simple, the results appear to represent the characteristics of the brown coal, at least volumetric change with moisture release process.

CONCLUSIONS

1. Change in conformation of Yallourn coal model simulated by CAMD method well correspond to the observed volumetric changes of the coal
2. Removal of water molecules results in a drastic conformational change in the final stage of moisture removal.
3. Re-adsorption of water molecules causes increase in coal volume without affecting the coal conformation.

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C:65.6, H:5.2, O:29.2 wt%

Mw:384.37

H-bond acceptor:7, H-bond donor:3

Figure 1 Unit structure assumed for YL model molecule.

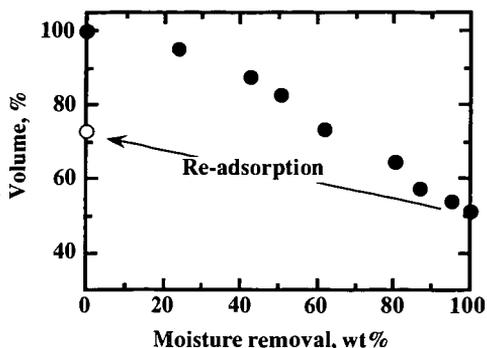


Figure 2 Volumetric change of YL during moisture release and re-adsorption process.

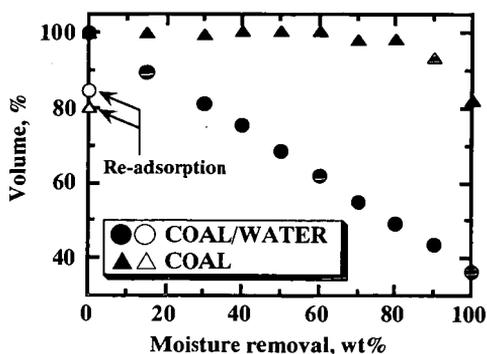


Figure 3 Volumetric change in YL model molecule with (COAL/WATER) and without (COAL) water molecules obtained with CAMD calculation.

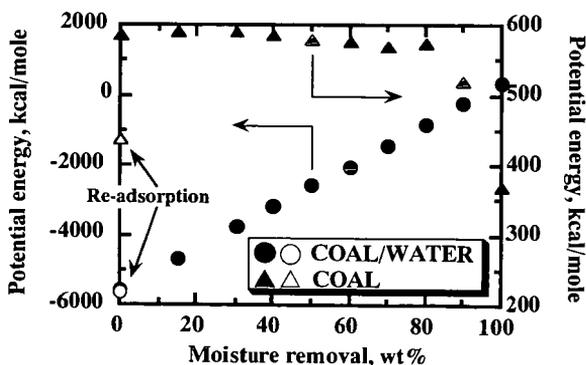


Figure 4 Variation in potential energies for YL model molecule with (COAL/WATER) and without (COAL) water molecules as a function of moisture removal.